

PATENT SPECIFICATION

922,021

NO DRAWINGS.

Inventors:—RAYMOND LAIT and DENNIS RICHARD LLOYD-OWEN.

Date of filing Complete Specification : Dec. 16, 1959.

Application Date : Jan. 22, 1959. No. 2432/59.

Complete Specification Published : March 27, 1963.



Index at Acceptance:—Classes 82, I4A(2:3B:3C:4B:4X), I(6:15); and 1(2), AC4A, AD10, AG25D10.

International Classification:—C22b (C01c, g).

COMPLETE SPECIFICATION.

Recovery of Palladium from Catalysts.

We, LAPORTE CHEMICALS LIMITED, a British Company, of Kingsway, Luton, Bedfordshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the recovery of palladium from used catalysts. More particularly it is applicable to the recovery of palladium from catalysts in which the palladium is supported on a carrier. The invention finds particular application in the case of catalysts which have been used in the catalytic reduction of alkylated or arylated anthraquinones to alkylated or arylated anthraquinols, and the application thereof to the manufacture of hydrogen peroxide. The invention will therefore be described more particularly with reference to said catalysts.

It is already well known that hydrogen peroxide can be manufactured by a process employing the autoxidation of certain organic compounds. Thus, for example, Specification No. 465,070 describes a process for the production of hydrogen peroxide in which an alkylated anthraquinone is hydrogenated in a solvent by means of hydrogen in the presence of a catalyst, to the corresponding alkylated anthraquinol, which after separation of the catalyst, is oxidised with oxygen to produce hydrogen peroxide with regeneration of the alkylated anthraquinone. The process is thus cyclic as the alkylated anthraquinone is recycled to the hydrogenation stage after removal of the hydrogen peroxide by, for example, aqueous extraction.

Various catalysts have been proposed for use in the reduction stage, one of the most usual being palladium though the use of Raney nickel has also been proposed. When palladium is used as the reduction catalyst it is usually supported on a carrier. Many carriers have been proposed such as alumina, magnesia, titania, charcoal, porous cement, calcium phosphate, and siliceous materials.

For example, our Specification No. 746,385 describes a process for the production of alkylated or arylated anthraquinhydrones or alkylated or arylated anthraquinols from alkylated or arylated anthraquinones and the application thereof to the manufacture of hydrogen peroxide wherein an alkylated or arylated anthraquinone in solution in a solvent or solvent mixture is reduced by means of hydrogen in the presence of a palladium catalyst material comprising metallic palladium deposited on a siliceous carrier which has been treated with an aqueous solution of an alkali.

Our Specification No. 760,737 describes a process for the reduction of anthraquinones in a solvent or solvent mixture by means of hydrogen in the presence of a palladium catalyst material consisting of metallic palladium supported on a silica-alumina carrier, this catalyst having been prepared by impregnating the carrier with a palladium compound by adsorption from an aqueous solution of a palladium salt, preferably a palladium nitrate or chloride solution, and then after adsorption of the palladium and removal of the catalyst from the aqueous solution treating the catalyst with an aqueous alkaline solution followed by reduction of

the palladium content of the catalyst to the metallic state.

During continued use of these catalysts their activity may fall and it is an object of this invention to provide a process for the recovery of palladium from used catalysts, especially from those used in the hydrogenation stage of the process for the production of hydrogen peroxide by the cyclic reduction and oxidation of alkylated or arylated anthraquinones. Palladium removed by the process of this invention may then be re-used.

Accordingly the present invention provides a process for the recovery of palladium from catalysts comprising palladium supported on a carrier the activity of which catalyst has been lost or decreased by use which comprises stripping the palladium from the support by slurrying in hydrochloric acid and passing in chlorine gas to form a palladium-containing solution, removing where necessary any material which is not made soluble by the action of the hydrochloric acid and chlorine gas, adding a metal which is more electro-positive than palladium to the palladium-containing solution to precipitate palladium metal, and removing the palladium metal so precipitated, for example, by filtration.

According to a preferred embodiment of the invention a process is provided for the recovery of palladium from hydrogenation catalysts the activity of which has been lost or decreased by use in a hydrogen peroxide-producing cycle involving the hydrogenation of alkyl or aryl substituted anthraquinones in the presence of a carrier-supported palladium catalyst which comprises stripping the palladium from the support by slurrying in hydrochloric acid and passing in chlorine gas to form a palladium-containing solution, removing where necessary any material which is not made soluble by the action of the hydrochloric acid and chlorine gas, adding a metal which is more electropositive than palladium to the palladium-containing solution to precipitate palladium metal, and removing the palladium metal so precipitated, for example, by filtration.

It is preferred to use as the added metal one which does not give rise to a coloured solution.

Preferably the metal which is more electro-positive than palladium is aluminium or magnesium.

Preferably the process is applied to palladium supported on siliceous or alumina-containing material.

Preferably the siliceous material is silica, silica gel, silica alumina, or an artificial aluminosilicate such as sodium aluminium silicate.

Preferably the alumina-containing material is alumina or activated alumina.

Preferably after removal of the carrier-supported palladium catalyst from the hydrogenation vessel the catalyst is washed with one or more organic solvents to remove at least in part any adherent organic material.

Preferably adhering solutions of alkyl substituted anthraquinones in solvents therefor are removed at least in part by washing with a hydrocarbon solvent having an atmospheric boiling point not exceeding 200° C.

Preferably such a hydrocarbon solvent is an aromatic hydrocarbon such as benzene or an alkyl benzene, which is used as a component of the solvent mixture in the autoxidation process.

Preferably solvents used to wash the carrier-supported palladium catalyst are removed by steam heating which may be followed by treatment of the catalyst with an alkaline reducing agent.

Alternatively adhering organic material may be removed by heat treatment in air which may be followed by treatment of the catalyst with an alkaline reducing agent.

Preferably palladium recovered in accordance with this invention is re-used to make further carrier-supported palladium catalyst.

If desired, the purity of the palladium recovered in accordance with this invention may be improved by redissolving the palladium in hydrochloric acid into which chlorine is passed, precipitating with concentrated ammonium solution impurities such as insoluble hydroxides or basic salts whilst retaining the palladium in solution as its tetra-ammino dichloride, filtering off the insoluble hydroxides followed by acidification to precipitate dichlorodiammine palladium and decomposition of this complex to yield metallic palladium.

As stated above the palladium is usually employed as a supported catalyst using porous supports such as alumina, silica-alumina, silica-gel, sodium aluminium silicate, titanium dioxide, magnesium hydroxide, charcoal or calcium phosphate. During use the activity of these catalysts declines and although reactivation is possible by known methods, eventually it is necessary to replace the catalyst. The palladium is valuable and must be recovered even if sometimes the support is discarded. Frequently this method of recovering palladium is applied to materials which may contain some catalyst but also large quantities of foreign material, e.g. catalyst fines, filter aid and other inert material which may contain no precious metal.

The process of the present invention provides a novel means for the recovery and purification of this palladium. After removal from the hydrogenator the spent catalyst may be washed with solvents to recover quinones and steam heated to remove the

solvents. The catalyst may then be washed with an alkaline reducing agent. This has two functions, (1) cleaning the catalyst and (2) reducing any partially oxidised palladium back to the metal. Alternatively the catalyst may be cleaned by heat treatment in a current of air, followed by reduction as described above.

The palladium is then stripped from the used catalyst by slurring in a hydrochloric acid solution and passing in chlorine gas. The palladium is recovered from the acid solution containing palladium chloride by addition of a metal which is more electropositive than palladium e.g. aluminium. By this means the palladium is obtained in a granular, easily filtered form. Finally it may be washed free of undesirable organic impurities with caustic soda solution.

As is shown in the following examples this novel process provides a means of recovering palladium from used catalyst in excellent yield. However, sometimes the purity of the recovered palladium is poor. This may be restored by the addition of an extra purification stage as described in Examples 4 and 5.

The recovered palladium can then be brought into solution again in hydrochloric acid by passing chlorine gas through the solution and used again for the preparation of new catalyst as described in Examples 1 to 5.

The following examples illustrate the invention.

EXAMPLE 1.

500 gms. of deactivated palladium on activated alumina catalyst, containing 9.8 gms. of palladium metal, was washed with xylene, filtered and sucked dry on a Buchner filter, and heated in a live steam oven at 90° C. for some hours to remove the remaining xylene. The dried xylene-washed catalyst was then stirred with 2 litres of hot aqueous sodium hydroxide solution containing 4 gms. of sodium hydroxide per litre, together with 250 ml. of 40% formaldehyde solution, to ensure that all the palladium was reduced to the metallic state, and to remove any remaining organic impurities from the catalyst.

This reduced catalyst was then stirred with 1500 ml. of 8N hydrochloric acid for nine hours whilst chlorine gas was bubbled through the mixture at an approximate rate of 2 ml. per second. No external heat was supplied. The mixture was then filtered, and the stripped alumina support washed with water until the washings were colourless. The alumina support was then washed with aqueous sodium hydroxide solution containing 40 gms. of sodium hydroxide per litre, followed by more water-washing, and then dried at 120° C. overnight. A portion of the support was analysed for pal-

ladium content. Analysis showed the stripped alumina to have 0.24 gm. of palladium remaining upon it.

The filtrate and washings were combined, and the palladium precipitated from solution by immersing a sheet of 99.5% aluminium in the palladium chloride solution. The precipitated palladium was filtered off, washed with water, then with 2% aqueous sodium hydroxide solution and finally with water until the washings were colourless and neutral in reaction. The crude palladium was dried, and then stirred with 22 ml. of 35% hydrochloric acid whilst chlorine gas was bubbled through the suspension, until all the palladium had dissolved. The solution was cooled, filtered, and diluted with water to a concentration appropriate for use in catalyst making. The solution contained 9.56 gms. of palladium as palladium chloride.

By the above process, 97.6% of the palladium was removed from the original palladium on alumina catalyst, the remaining 2.4% of the palladium remaining upon the support. No other loss of palladium was observed during the stripping operation.

The dried stripped alumina and palladium solution both obtained as detailed above, were taken, and fresh catalyst made with them substantially according to the process described in Example 1 of our United Kingdom Specification No. 718,306.

The catalyst obtained was as good in activity and performance as that obtained with catalyst made in a similar manner using solutions of fresh palladium, and new or stripped alumina support.

EXAMPLE 2.

12.4 kgms. of deactivated palladium on an artificial sodium aluminosilicate catalyst, containing 143 gms. of palladium metal, was xylene-washed, filtered, sucked dry, and heated in a live steam oven for some hours. The catalyst material, now weighing 9.1 kgms. was stirred with 32 litres of 2% aqueous sodium hydroxide solution together with 600 ml. of 40% formaldehyde solution at 60° C. for one hour. The suspension was then cooled, filtered, washed with water until free of alkali and finally sucked dry on the filter. The moist cleaned reduced catalyst was stirred at 60° C. for nine hours with 27 litres of 35% commercial hydrochloric acid whilst gaseous chlorine was bubbled through the mixture at a rate of 15 ml./second. At the end of this time, the mixture was cooled to 40° C. and filtered. The sodium aluminium silicate support was washed until the washings were colourless and then the support was discarded to waste, after the residual palladium content had been checked (0.1% palladium).

The filtrate and washings were combined

and the palladium precipitated from solution by the immersion in the solution of a piece of 99.5% aluminium sized about 30.5 cms. \times 30.5 cms. \times 1.9 cms. The precipitated palladium was filtered off, washed with water, 4.5 litres of 2% aqueous sodium hydroxide solution and finally with more water until the washings were water-white and neutral. The crude palladium, containing 140 gms. of palladium, was dried at 120° C. powdered to give <20 mesh B.S.S. particles and stirred with 300 ml. of concentrated hydrochloric acid, whilst chlorine gas was bubbled through for four hours, when all the palladium had gone into solution. The solution was cooled, filtered, and diluted with water to give a palladium concentration appropriate for use in catalyst manufacture.

By the above-detailed process, 97.9% of the palladium was recovered from the original spent catalyst, the remaining 2.1% (3 gms.) of the palladium being lost upon the stripped support, in the liquors, and in handling.

New artificial sodium aluminium silicate support was taken, sieved to give -100 +240 mesh B.S.S. particles, and palladised, using the above mentioned palladium chloride solution substantially by the process described in Example 4 of United Kingdom Specification No. 746,385.

The activity of the catalyst manufactured from this recovered palladium was as good as that obtained with catalyst made by the same process from new palladium and the same support.

EXAMPLE 3.

Palladium chloride solution prepared from palladium successfully recovered from spent palladium on an artificial sodium aluminosilicate catalyst substantially in the same manner as described in Example 2 was used in the making of palladium on sodium aluminosilicate catalyst substantially as in the way disclosed in Example 4 in our co-pending Application No. 2433/59 (Serial No. 922,022).

The activity and performance of the result-catalyst was in every way as good as that obtained with catalyst made by the same process from a new palladium and the same support.

EXAMPLE 4.

61.3 kgms. of spent palladium on silica-alumina catalyst, having 42% by weight of material volatile at 400° C. was contacted with 91 litres of xylene and stirred at room temperature for 90 minutes. The washed catalyst was then filtered off, sucked dry and placed on trays in a steam oven where live steam was passed over the catalyst for several hours.

The dry xylene-washed catalyst, now weighing 42.7 kgms. and containing 12.2% of material volatile at 400° C. and 712 gms.

of metallic palladium, was stirred at 60° C. for an hour with 182 litres of 5% aqueous sodium hydroxide solution together with 3375 ml. of 40% formaldehyde solution. After this time, the mixture was cooled to <40° C., filtered, the filter-cake water-washed until the washings came through colourless and then sucked dry. The red-black filtrate was run to waste.

The catalyst was then stirred at 70°—80° C. for 3 hours with 114 litres of commercial 35% hydrochloric acid, whilst gaseous chlorine was bubbled through the suspension at a rate of 40 ml. per second. The mixture was then cooled to <40° C., filtered, and the filter-cake washed five times with water, using approximately 23 litres of water per wash. The stripped support was discarded after the residual palladium content had been checked (<0.1% palladium). The washings and filtrate were combined, and the palladium precipitated from solution by immersing a 30.5 cms. \times 30.5 cms. \times 1.9 cms. sized piece of 99.5% aluminium in the dilute palladium chloride solution. The precipitated palladium was filtered off, washed with water, 18.2 litres of 2% aqueous sodium hydroxide solution, followed by more water until the washings were colourless and neutral.

The crude palladium, after drying at 120° C. contained 702 gms. of palladium, but was only 85% pure, also having 3% of aluminium, 1% of silicon, 1% of copper, 1% of lead, 1% of iron, and other metallic contaminants in less proportions.

Accordingly, the crude palladium was purified in the following manner. The crude palladium was powdered to <20 mesh B.S.S. particles, suspended with stirring in 1,500 ml. of 35% hydrochloric acid whilst gaseous chlorine was passed through the mixture for five hours at an approximate rate of 12 ml. per second. The mixture was then cooled, filtered, and the residue well-washed with water. The residue, dried weight 27 gms. contained only 0.2 gm. of palladium, and consisted to a large extent of silica with some alumina. The filtrate and washings were combined and 5 litres of 0.880 ammonium hydroxide solution added carefully. The initial flesh-coloured precipitate of a palladium complex was redissolved to give the soluble palladium tetra-amminodichloride ($\text{Pd}(\text{NH}_3)_4\text{Cl}_2$) by warming the mixture for a short time. The precipitated impurities, mostly hydroxides or basic salts of lead, iron and aluminium, together with traces of palladium were filtered off, the residue well washed and then discarded. The combined filtrate and washings were acidified with 2.2 litres of 35% hydrochloric acid, causing the precipitation of the yellow compound, dichlorodiammine palladium ($\text{Pd}(\text{NH}_3)_2\text{Cl}_2$).

This yellow precipitate was filtered off, and well washed with water. The filtrate and washings containing the remaining impurities mostly copper with traces of palladium were discarded.

The yellow precipitate was slurried with 3.5 litres of water, and a prepared solution, consisting of 840 ml. of 80% w/w hydrazine hydrate made up to 3.5 litres with water, was slowly added to the slurry. The complex was immediately decomposed, liberating metallic palladium. After warming to complete the decomposition and coagulate the palladium, the palladium was filtered off, washed with 16 litres of water, sucked dry, and dried at 120° C. The percentage purity of the resulting palladium was 99.9% and only 3.2 gm. or less than 0.5% of the palladium was lost during the above described purification.

The purified palladium was brought into solution as palladium chloride by stirring with 1,500 ml. of 35% hydrochloric acid for five hours whilst gaseous chlorine was bubbled through the mixture at an approximate rate of 12 ml. per second. The solution was cooled, and diluted with water to give a palladium concentration appropriate for use in catalyst manufacture.

By the above process, 98.3% of the palladium was recovered from the original spent catalyst in a very pure form.

New silica-alumina support was taken, sieved to give -100 +240 mesh B.S.S. particles and palladised substantially by the process described in Example 6 of our co-pending Application No. 2433/59 (Serial No. 922,022).

The activity and performance of the catalyst made from this purified recovered palladium was as good as that obtained with catalyst made in substantially the same manner with the same support and new palladium.

EXAMPLE 5.

Crude palladium metal was successfully recovered from spent palladium on silica-alumina catalyst in substantially the same manner as in Example 4.

The crude palladium metal was converted into the yellow precipitate of dichlorodiammine palladium ($\text{Pd}(\text{NH}_3)_2\text{Cl}_2$) in substantially the same manner as in Example 4. This precipitate was then heated at 400° C. in an atmosphere of hydrogen to give sponge palladium metal. This palladium was converted into palladium chloride in solution in substantially the same manner as in Example 4, and the solution, diluted appropriately, was used in the making of palladium on silica-alumina catalyst substantially by the process described in Example 5 of our Specification No. 760,737.

The activity and performance of the resulting catalyst was in every way as good as that

obtained with catalyst made by the same process from new palladium and the same support.

WHAT WE CLAIM IS:—

1. A process for the recovery of palladium from catalysts comprising palladium supported on a carrier the activity of which catalyst has been lost or decreased by use, which comprises stripping the palladium from the support by slurrying in hydrochloric acid and passing in chlorine gas to form a palladium-containing solution, removing where necessary any material which is not made soluble by the action of the hydrochloric acid and chlorine gas, adding a metal which is more electropositive than palladium to the palladium-containing solution to precipitate palladium metal, and removing the palladium metal so precipitated, for example by filtration.

2. A process for the recovery of palladium from hydrogenation catalysts the activity of which has been lost or decreased by use in a hydrogen peroxide-producing cycle involving the hydrogenation of alkyl or aryl substituted anthraquinones in the presence of a carrier-supported palladium catalyst, which comprises stripping the palladium from the support by slurrying in hydrochloric acid and passing in chlorine gas to form a palladium-containing solution, removing where necessary any material which is not made soluble by the action of the hydrochloric acid and chlorine gas, adding a metal which is more electropositive than palladium to the palladium-containing solution to precipitate palladium metal, and removing the palladium metal so precipitated, for example, by filtration.

3. A process as claimed in Claim 2 wherein, prior to the acid slurrying step, the carrier-supported palladium catalyst is first washed with one or more organic solvents, preferably xylene, then steam heated to remove the solvent or solvents and then washed with an alkaline reducing agent.

4. A process as claimed in any one of the preceding claims wherein the carrier-supported palladium catalyst comprises palladium supported on siliceous or alumina-containing material.

5. A process as claimed in Claim 4 wherein the siliceous material is silica, silica gel, silica alumina, or an artificial aluminosilicate such as sodium aluminium silicate.

6. A process as claimed in Claim 4 wherein the alumina-containing material is alumina or activated alumina.

7. A process as claimed in any one of the preceding claims, wherein there is employed as the added metal one which does not give rise to a coloured aqueous solution.

8. A process as claimed in Claim 7 wherein the added metal is aluminium.

9. A process as claimed in Claim 7 wherein the added metal is magnesium.

10. Palladium whenever recovered by a process claimed in any one of the preceding claims.

11. A process for the recovery and purification of palladium from catalysts comprising palladium supported on a carrier substantially as described with reference to any one of the examples.

12. Palladium when obtained by the process claimed in Claim 11.

13. A process for the purification of the palladium claimed in Claim 10 comprising the steps of dissolving the palladium in hydrochloric acid into which chlorine is passed, precipitating with concentrated ammonia solution impurities such as insoluble hydroxides or basic salts whilst re-

taining the palladium in solution as its tetra-ammino dichloride, filtering off the insoluble hydroxides followed by acidification to precipitate dichlorodiammine palladium and decomposition of this complex to yield metallic palladium.

14. A process as claimed in Claim 13 wherein the complex is decomposed by the addition thereto of an aqueous solution of hydrazine hydrate.

15. Palladium when obtained by the process claimed in Claim 13 or 14.

ELKINGTON & FIFE,
Consulting Chemists
and Chartered Patent Agents,
Bank Chambers, 329 High Holborn,
London, W.C.1,
Agents for the Applicants.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1963.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.